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Light Harvesting

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White-Light-Emitting Supramolecular Gels**

*Vakayil K. Praveen, Choorikkat Ranjith, and Nicola Armaroli**

energy transfer · gels · light harvesting · self-assembly · white-light emission

White-light-emitting organic materials are gaining increasing attention in contemporary research owing to their potential for application in electroluminescent devices and sensors.[1] In general, white-light-emitting systems are composed of components (single or multiple) that emit either the three primary (red, green, and blue) or two complementary colors (e.g. orange and turquoise) to cover the entire visible spectral window (380–750 nm).[1] The management of energy-transfer processes within or between the components is crucial for white-light (WL) emission and is possible by proper molecular design and by the control of intercomponent interactions in solution or in the solid state.[1] In this context, supramolecular gels formed by the spontaneous self-assembly of molecules are privileged media that exhibit properties both of the solution and of the solid state.[2] The practical relevance of this approach lies in the ability of the gel matrix to accommodate the luminescent components as donors or acceptors of excitation energy; this capacity ultimately controls the efficiency of the energy-transfer process.[2c,d] Herein we highlight some examples of chromophore-based gels as scaffolds for the assembly of WL-emitting soft materials.

A WL-emitting organogel based on the controlled self-assembly of the energy donor was demonstrated by Ajayaghosh and co-workers.[3a] The difference in molecular packing of the cholesterol-functionalized oligo(*p*-phenylene vinylene) (OPV) donors (Figure 1) in the twisted (compound **1**) or coiled helices (compound **2**) influences the migration of the excitation energy. Because of weak gelation and slow exciton diffusion, only partial energy transfer (63 %) occurred from the aggregates of **1** to the red-light-emitting acceptor **3** added as dopant (Figure 1), yielding WL emission (Commission Internationale de l'Éclairage, CIE 1931 color coordinates: $x = 0.31$, $y = 0.35$; Figure 1 a).[3a] Such emission is a combination of the red output of the acceptor and the blue and green emission from the monomers and aggregates, respectively, of the partially quenched donor. In contrast, the strong gelation and fast exciton diffusion of **2** facilitated efficient energy transfer (90 %) and led to red emission from the acceptor.[3]

Schenning and co-workers thoroughly designed and synthesized a series of self-assembling fluorene-based co-oligomers **4**–**7** with tunable emission properties (Figure 1).[4] The mixing of these molecules with different emission colors, **5** (green), **6** (yellow), and **7** (red), into a gel of **4** in a 0.7:0.2:0.1:4.5 molar ratio (**5**/**6**/**7**/**4**) resulted in partial photoinduced energy transfer from the blue-emitting donor to the acceptors and thus led to a WL-emitting gel.

In an elaborate study, Del Guerzo and co-workers demonstrated the preparation of WL-emitting gel nanofibers and their characterization by confocal fluorescence microscopy.[5] For this purpose, they used a blue-emitting gel of 2,3-bis(decyloxy)anthracene (**8**; Figure 1) as the light-harvesting scaffold capable of hosting and sensitizing the acceptors. The green- and red-emitting tetracene-based acceptors **9** and **10** (Figure 1) were specifically designed to display emission in the low-energy region and to have good luminescence quantum yields and structural similarities with the donor. WL emission is obtained through control of the efficiency of energy transfer from the donor to the acceptors by adjusting the doping ratio in the coassembled gel. Thus, the addition of **9** (0.012 equiv) and **10** (0.012 equiv) to **8** resulted in WL emission with the CIE coordinates 0.32, 0.33. Detailed confocal fluorescence microscopy studies unambiguously proved that WL emission from the self-assembled nanofibers (Figure 1 b) was due to partial energy transfer from the donor to the acceptors.[5a] In a separate study, the energy-transfer processes responsible for color tuning and WL emission were studied in detail.[5b] With the help of steady-state and time-resolved emission spectroscopy, the involvement of several processes was evidenced: 1) direct **8**→**9** and **8**→**10** energy transfer, 2) stepwise **8**→**9**→**10** energy transfer, and 3) **8**→**8** excitation-energy hopping. Clearly, the success of this design relies on the high-level ordering of molecules in the gel fiber network to facilitate energy migration in a controlled fashion.

Yi and co-workers reported a WL-emitting supramolecular gel composed of a naphthalimide-based gelator **11** (donor) and a phosphorescent Ir^{III} complex **12** (acceptor; Figure 2).[6] Morphological analysis showed that **12** formed nanoparticles that were well-dispersed within the gel matrix of **11**. Luminescence studies showed that, depending on the

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[*] Dr. V. K. Praveen, Dr. N. Armaroli
Istituto per la Sintesi Organica e la Fotoreattività
Consiglio Nazionale delle Ricerche (ISOF-CNR)
Via Gobetti 101, 40129 Bologna (Italy)
E-mail: nicola.armaroli@isof.cnr.it
Homepage: http://www.isof.cnr.it/?q=content/armaroli-nicola

Dr. C. Ranjith
Dipartimento di Chimica Organica, Università degli Studi di Milano
Via Golgi 19, 20133 Milano (Italy)

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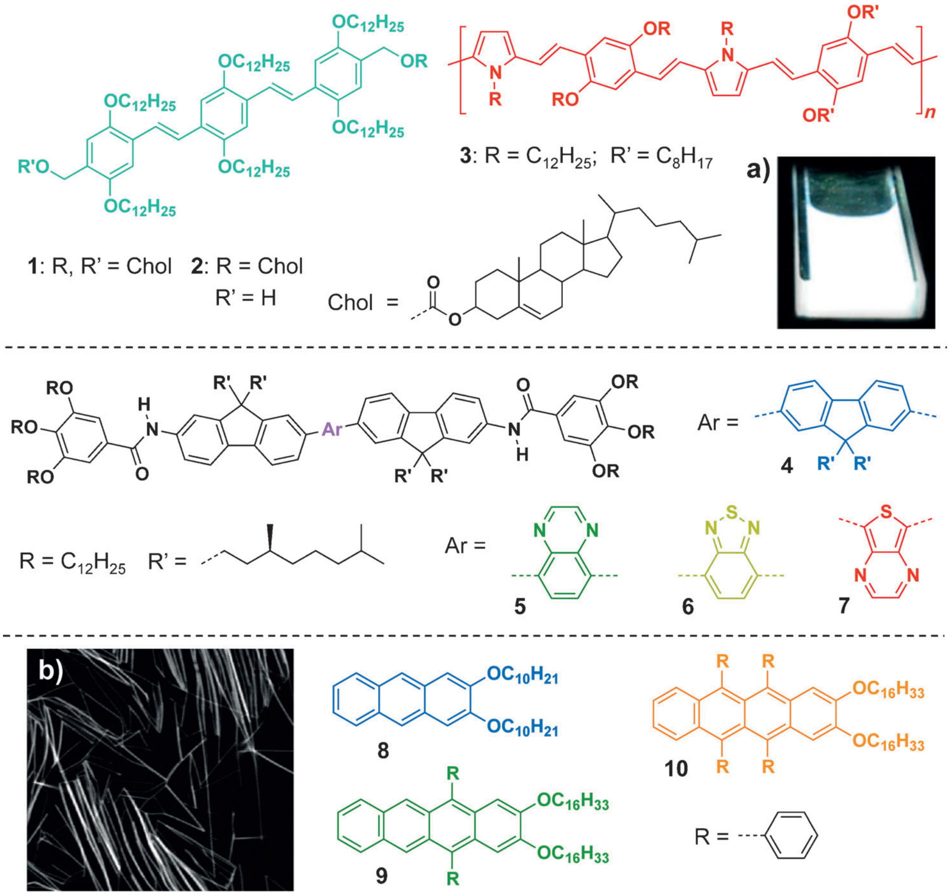

Figure 1. Molecular structures of energy-transfer donors and acceptors used for the design of WL-emitting supramolecular gels. a) Photograph of a WL-emitting gel (**1** + **3**). b) Fluorescence-intensity confocal microscopy image of a WL-emitting gel (**8** + **9** + **10**). Images (a) and (b) were reproduced with permission from Refs. [3a] and [5a], respectively.

molar ratio of the donor and acceptor, partial quenching of the blue emission from **11** and orange luminescence from **12** resulted in emission with CIE coordinates in the WL region. The morphology of the mixed gel and the optical properties of the donor scaffold and encapsulated acceptor are considered to be the key factors in controlling the efficiency of the energy-transfer process. These authors also successfully demonstrated the usefulness of the WL-emitting gel as a sensor by exploiting the interaction of cysteine with the Ir^{III} complex. In the presence of cysteine, the WL-emitting gel showed a clear spectral shift towards the blue that could be detected by the naked eye.

Nandi and co-workers extensively investigated the gelation and morphological properties of a hydrogen-bonding complex of melamine (**13**) and 6,7-dimethoxy-2,4[1*H*,3*H*]-quinazolinedione (**14**; Figure 2).[7] The blue-emitting gel formed from **13** + **14** underwent efficient energy transfer to a doped acceptor, such as riboflavin (**15**; Figure 2) to afford a green fluorescent gel.[7a] In a recent study, they further showed that the addition of rhodamine B (**16**; Figure 2) to the above system tunes the emission towards white (CIE coordinates: 0.31, 0.36).[7b] Thus, a coassembled gel containing 0.5 mol % of **15** and 0.02 mol % of **16** with respect to **13** + **14** showed a broad emission with peaks corresponding to **14**, **15**, and **16**. This result underpins the occurrence of energy transfer from **14** to **15**, **14** to **16**, and **15** to **16**.

The photophysical properties of metal complexes make them attractive for integration in soft materials.[2e] Kim and Chang utilized this idea to obtain a WL-emitting metallogel consisting of the Tb^{III} and Eu^{III} phenanthroline complexes **17** and **18** as gelators (Figure 2).[8] The presence of the same kind of ligand allowed perfect mixing of **17** and **18**. At a 19:1 weight ratio of **17** and **18**, WL emission (CIE coordinates: 0.36, 0.30) was observed as a result of the balancing of ligand-centered bluish emission by the green and red emissions from Tb^{III} and Eu^{III} ions, respectively.

In a recent report, Eswaramoorthy, George, and co-workers described the design of a WL-emitting soft hybrid gel composed of amine-functionalized organoclay (**AC**) and anionic dyes.[9] The donor and acceptor chromophores used in this study were the blue-emitting coronene tetracarboxylate **19** and sulforhodamine G (**20**) with yellow fluorescence, respectively (Figure 2). The mixing of **AC** and bifunctional **19** in water resulted in extended supramolecular assembly and gelation. Upon doping with **20**, the coassembled gel showed partial quenching of the fluorescence of **19** along with emission from **20**, indicating transfer of excitation energy. The highly transparent gel can be coated on any surface owing

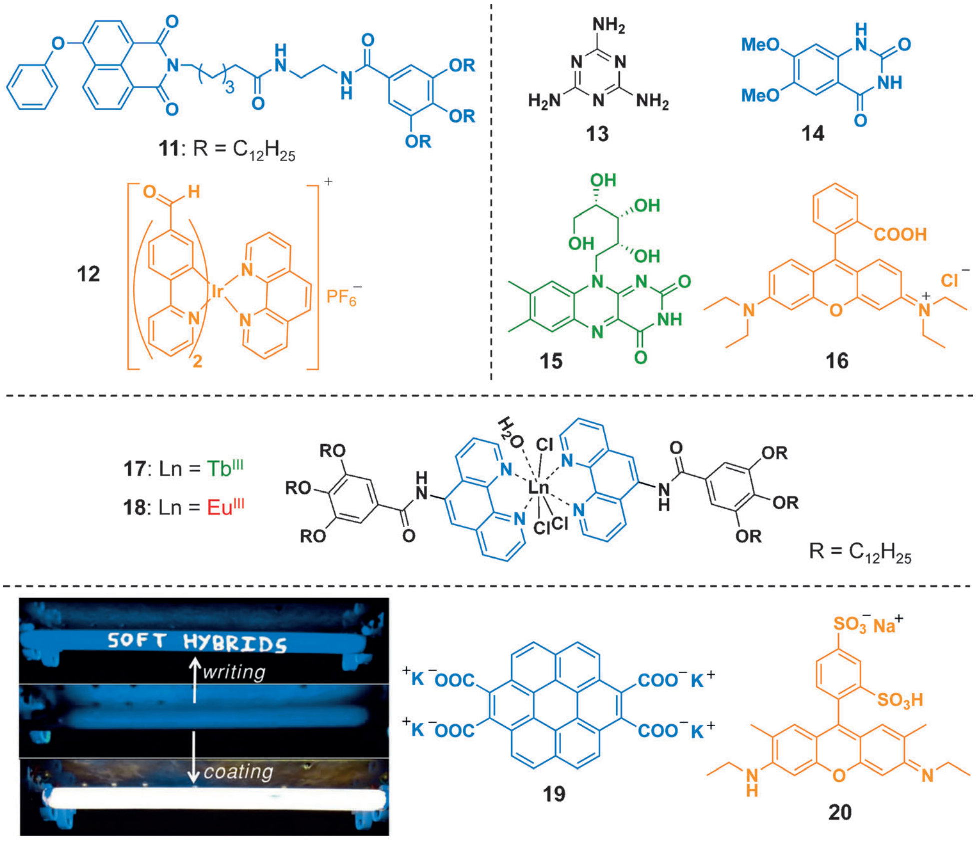

Figure 2. Molecular structures of energy-transfer donors and acceptors used for the design of WL-emitting supramolecular gels. The bottom-left picture (reproduced with permission from Ref. [9]) shows the use of the **19**–**AC**–**20** hybrid gel as a coating for tube lamps: upon UV irradiation by the tube, a bright WL output is obtained from partially (written letters) and fully coated lamps.

to its thixotropic and soft character (Figure 2). A film thus prepared displayed pure WL emission (CIE coordinates: 0.33, 0.32) when 0.65 mol% of the acceptor was loaded, which resulted in 70% quenching of donor emission. The processability along with the ability to retain the color purity of WL in the xerogel state makes this approach very promising for future applications.

By means of fluorescence microscopy, Lu and co-workers demonstrated an energy-transfer-mediated purplish WL emission from a coassembled gel composed of a blue-emitting carbazole gelator and a diaryl diketopyrrolopyrrole derivative as a dopant.[10]

A temperature-dependent gel–sol transition leading to WL emission was reported for a system composed of a bishydroxy OPV derivative and **3**.[3b] Upon heating, the OPV gel assembly broke down into a mixture of monomers and aggregates, reducing the extent of energy transfer from the latter to acceptor **3**. In a particular temperature range (50–60 °C), the combination of the blue emission of the monomer, the sensitized red emission of the acceptor, and the residual green emission of the aggregates generated WL luminescence. In another study, the color tuning of a hydrogelator based on a phenylenedivinylenebis(*N*-octylpyridinium) salt by the addition of NaBr led to WL emission in solution.[11] By varying either the temperature or the concentration of NaBr, the extent of aggregation and the emission properties could be fine-tuned.

Besides the aforementioned selected methods, many promising approaches for WL-emitting soft materials based on supramolecular polymers,[12] vesicles,[13] micelles,[14] organic[15] and silica[16] nanoparticles, 1D nanostructures,[17] DNA assemblies,[18] solvent-free liquids,[19] and organic–inorganic hybrids[20] have been developed in recent years. We have focused herein on some recent significant developments in WL-emitting gels. The availability of a variety of chromophores as gelators along with their ease of preparation and processability can make supramolecular gels technologically friendly soft materials. However, their use in real devices has yet to be explored; efficiency and durability are major constraints to be overcome. In the coming years, we can expect substantial developments in this direction, with efforts to make WL-emitting supramolecular gels a truly viable choice as active materials for optoelectronic devices, particularly in the lighting-technology sector.

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[1] For reviews, see: a) H. Wu, L. Ying, W. Yang, Y. Cao, *Chem. Soc. Rev.* **2009**, *38*, 3391–3400; b) K. T. Kamtekar, A. P. Monkman, M. R. Bryce, *Adv. Mater.* **2010**, *22*, 572–582; c) G. M. Farinola, R. Ragni, *Chem. Soc. Rev.* **2011**, *40*, 3467–3482.

[2] For reviews, see: a) T. Ishi-i, S. Shinkai, *Top. Curr. Chem.* **2005**, *258*, 119–160; b) S. Yagai, *J. Photochem. Photobiol. C* **2006**, *7*,

164–182; c) A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, *Chem. Soc. Rev.* **2008**, *37*, 109–122; d) S. S. Babu, K. K. Kartha, A. Ajayaghosh, *J. Phys. Chem. Lett.* **2010**, *1*, 3413–3424; e) L. Maggini, D. Bonifazi, *Chem. Soc. Rev.* **2012**, *41*, 211–241; f) A. Y.-Y. Tam, V. W.-W. Yam, *Chem. Soc. Rev.* **2013**, *42*, 1540–1567.

[3] a) C. Vijayakumar, V. K. Praveen, A. Ajayaghosh, *Adv. Mater.* **2009**, *21*, 2059–2063; b) A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, S. J. George, *Angew. Chem.* **2007**, *119*, 6376–6381; *Angew. Chem. Int. Ed.* **2007**, *46*, 6260–6265; c) C. Vijayakumar, V. K. Praveen, K. K. Kartha, A. Ajayaghosh, *Phys. Chem. Chem. Phys.* **2011**, *13*, 4942–4949.

[4] R. Abbel, R. van der Weegen, W. Pisula, M. Surin, P. Leclère, R. Lazzaroni, E. W. Meijer, A. P. H. J. Schenning, *Chem. Eur. J.* **2009**, *15*, 9737–9746.

[5] a) C. Giansante, G. Raffy, C. Schäfer, H. Rahma, M.-T. Kao, A. G. L. Olive, A. Del Guerzo, *J. Am. Chem. Soc.* **2011**, *133*, 316–325; b) C. Giansante, C. Schäfer, G. Raffy, A. Del Guerzo, *J. Phys. Chem. C* **2012**, *116*, 21706–21716.

[6] X. Cao, Y. Wu, K. Liu, X. Yu, B. Wu, H. Wu, Z. Gong, T. Yi, *J. Mater. Chem.* **2012**, *22*, 2650–2657.

[7] a) P. Bairi, B. Roy, A. K. Nandi, *Chem. Commun.* **2012**, *48*, 10850–10852; b) P. Bairi, B. Roy, P. Chakraborty, A. K. Nandi, *ACS Appl. Mater. Interfaces* **2013**, *5*, 5478–5485.

[8] H. Kim, J. Y. Chang, *RSC Adv.* **2013**, *3*, 1774–1780.

[9] K. V. Rao, K. K. R. Datta, M. Eswaramoorthy, S. J. George, *Adv. Mater.* **2013**, *25*, 1713–1718.

[10] X. Yang, R. Lu, P. Xue, B. Li, D. Xu, T. Xu, Y. Zhao, *Langmuir* **2008**, *24*, 13730–13735.

[11] S. Bhattacharya, S. K. Samanta, *Chem. Eur. J.* **2012**, *18*, 16632–16641.

[12] a) R. Abbel, C. Grenier, M. J. Pouderoijen, J. W. Stouwdam, P. E. L. G. Leclère, R. P. Sijbesma, E. W. Meijer, A. P. H. J. Schenning, *J. Am. Chem. Soc.* **2009**, *131*, 833–843; b) M. R. Molla, S. Ghosh, *Chem. Eur. J.* **2012**, *18*, 1290–1294; c) D. K. Maiti, A. Banerjee, *Chem. Commun.* **2013**, *49*, 6909–6911.

[13] a) X. Zhang, S. Rehm, M. M. Safont-Sempere, F. Würthner, *Nat. Chem.* **2009**, *1*, 623–629; b) K.-P. Tseng, F.-C. Fang, J.-J. Shyue, K.-T. Wong, G. Raffy, A. Del Guerzo, D. M. Bassani, *Angew. Chem.* **2011**, *123*, 7170–7174; *Angew. Chem. Int. Ed.* **2011**, *50*, 7032–7036.

[14] X. Zhang, D. Görl, F. Würthner, *Chem. Commun.* **2013**, *49*, 8178–8180.

[15] a) R. Abbel, R. van der Weegen, E. W. Meijer, A. P. H. J. Schenning, *Chem. Commun.* **2009**, 1697–1699; b) B. Balan, C. Vijayakumar, S. Ogi, M. Takeuchi, *J. Mater. Chem.* **2012**, *22*, 11224–11234; c) S. Kim, S.-J. Yoon, S. Y. Park, *J. Am. Chem. Soc.* **2012**, *134*, 12091–12097.

[16] a) M. Melucci, M. Zambianchi, G. Barbarella, I. Manet, M. Montalti, S. Bonacchi, E. Rampazzo, D. C. Rambaldi, A. Zattoni, P. Reschiglian, *J. Mater. Chem.* **2010**, *20*, 9903–9909; b) J. Malinge, C. Allain, A. Brosseau, P. Audebert, *Angew. Chem.* **2012**, *124*, 8662–8665; *Angew. Chem. Int. Ed.* **2012**, *51*, 8534–8537; c) F. Gai, T. Zhou, L. Zhang, X. Li, W. Hou, X. Yang, Y. Li, X. Zhao, D. Xu, Y. Liu, Q. Huo, *Nanoscale* **2012**, *4*, 6041–6049.

[17] a) X. Wang, J. Yan, Y. Zhou, J. Pei, *J. Am. Chem. Soc.* **2010**, *132*, 15872–15874; for a review, see: b) C. Zhang, Y. S. Zhao, J. Yao, *New J. Chem.* **2011**, *35*, 973–978; c) Y.-L. Lei, Y. Jin, D.-Y. Zhou, W. Gu, X.-B. Shi, L.-S. Liao, S.-T. Lee, *Adv. Mater.* **2012**, *24*, 5345–5351.

[18] a) R. Varghese, H.-A. Wagenknecht, *Chem. Eur. J.* **2009**, *15*, 9307–9310; b) K. S. Sanju, P. P. Neelakandan, D. Ramaiah, *Chem. Commun.* **2011**, *47*, 1288–1290.

[19] S. S. Babu, J. Aimi, H. Ozawa, N. Shirahata, A. Saeki, S. Seki, A. Ajayaghosh, H. Möhwald, T. Nakanishi, *Angew. Chem.* **2012**, *124*, 3447–3451; *Angew. Chem. Int. Ed.* **2012**, *51*, 3391–3395.

[20] For reviews, see: a) G. Calzaferri, K. Lutkouskaya, *Photochem. Photobiol. Sci.* **2008**, *7*, 879–910; b) N. Mizoshita, T. Tani, S. Inagaki, *Chem. Soc. Rev.* **2011**, *40*, 789–800; c) K. V. Rao, K. K. R. Datta, M. Eswaramoorthy, S. J. George, *Chem. Eur. J.* **2012**, *18*, 2184–2194.